



Effects of Pisha sandstone content on solute transport in a sandy soil



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HIGHLIGHTS

- Pisha sandstone can successfully impede solute transport in a sandy soil column.
- Pisha sandstone impeded the breakthrough of Br⁻ and Na⁺ by decreasing the saturated hydraulic conductivity.
- Pisha sandstone impeded the breakthrough of Na⁺ also by increasing the adsorption capacity of the soil.

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ABSTRACT

In sandy soil, water, nutrients and even pollutants are easily leaching to deeper layers. The objective of this study was to assess the effects of Pisha sandstone on soil solute transport in a sandy soil. The miscible displacement technique was used to obtain breakthrough curves (BTCs) of Br⁻ as an inert non-adsorbed tracer and Na⁺ as an adsorbed tracer. The incorporation of Pisha sandstone into sandy soil was able to prevent the early breakthrough of both tracers by decreasing the saturated hydraulic conductivity compared to the controlled sandy soil column, and the impeding effects increased with Pisha sandstone content. The BTCs of Br⁻ were accurately described by both the convection-dispersion equation (CDE) and the two-region model (T-R), and the T-R model fitted the experimental data slightly better than the CDE. The two-site nonequilibrium model (T-S) accurately fit the Na⁺ transport data. Pisha sandstone impeded the breakthrough of Na⁺ not only by decreasing the saturated hydraulic conductivity but also by increasing the adsorption capacity of the soil. The measured CEC values of Pisha sandstone were up to 11 times larger than those of the sandy soil. The retardation factors (R) determined by the T-S model increased with increasing Pisha sandstone content, and the partition coefficient (K_d) showed a similar trend to R. According to the results of this study, Pisha sandstone can successfully impede solute transport in a sandy soil column.

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1. Introduction

Studies of water movement and contaminant transport in soils are currently receiving increased attention (Al-Qinna et al., 2014). It has been reported that many contaminant transport solutes bypass the soil matrix, including pesticides (Xu et al., 1999; Hantush et al., 2000; Köhne et al., 2009; Larsbo et al., 2013; Prado et al., 2014), viruses (Sim and Chrysikopoulos, 2000; Ojha et al., 2011), nutrients such as nitrogen and phosphorus (Sinaj et al., 2002; Akhtar et al., 2003; Djodjic et al., 2004; Wang et al., 2013), and heavy metals such as Cd, Cu, Zn, and Pb (Lichner et al., 2006; Kim et al., 2008; Sayyad et al., 2010; Chotpantarat et al., 2012; Janetti et al., 2013).

These solutes may pose risks to the environment. Therefore, research on the behavior of solutes in soil is driven by the need to manage and prevent the possible means of contamination.

Soil texture and structure significantly impact water flow and the transport of contaminants in soils (Kodešová et al., 2009). Due to its homogeneous particle size and low percentages of silt and clay, sandy soil retains both water and nutrients poorly. Through a lysimeter experiment, Vogeler et al. (2006) showed that 60% of the nitrate content of sewage sludge was lost by leaching when applied to a sandy loam soil. Measures have therefore been taken to improve the physical qualities of coarse-textured soils, among which the application of various soil conditioners to soils is widely practiced. Both natural organic soil conditioners (Gupta et al., 1977; Schjønning et al., 1994; Lindsay and Logan, 1998; Nyamangara et al., 2001) and synthetic organic soil conditioners (Al-Darby, 1996) are applied to sandy and sandy loam soils, with these studies finding that the application of both types of soil conditioners

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can improve some of the physical qualities of soil, such as the soil water holding capacity.

The total area of Shanxi, Shaanxi and Inner Mongolia's border region in northwest China is 5.44×10^4 km², and the main soil types are aeolian sandy soil and loess soil, meanwhile, 1/3 of the area are distributed of loose rock known as Pisha sandstone (some people translate it as "Feldspathic Sandstone" or "Soft Rock"). Mu Us Desert is located in this region, and some studies found that the soil nutrients of this area were low and easy to lose (Wang et al., 2009). Pisha sandstone is a type of loose rock that is specifically identified as an interbedded sandstone composed of thick layers of sandstone, sandy shale and shale that formed in the Permian (approximately 250 million years ago), Triassic, Jurassic and Cretaceous (Yuanchang et al., 2007). It is a continental clastic sandstone series. The rock's history of low pressure conditions, which is due to the small thickness of overburden rock, results in a low degree of diagenesis, a low degree of sand cementation and poor structural strength (Yuanchang et al., 2007). However, the rock becomes muddy when exposed to water. As a result of its natural physical, chemical characters and the special local natural and cultural environment, it is easy to be eroded and the local people are deeply endured the hazards of its severe soil erosion. Chinese government attaches great importance to the controlling Pisha sandstone, and have launched a number of research and treatment projects in the region. Due to the properties of becoming muddy with water and a high content of montmorillonite, several studies have found that the incorporation of Pisha sandstones into sandy soils can significantly decrease the water infiltration rate, saturated hydraulic conductivity, and water loss through evaporation of the soil, while increasing the saturated water content and residual water content (Lu et al., 2014; She et al., 2014). Thus, Pisha sandstone were selected as soil amendments for sandy soil, and more than 1600 hm² new arable lands have been added by incorporating Pisha sandstone into sandy soils (Han et al., 2012). This showed that it is technically feasible to use Pisha sandstone as soil amendment in this area. However, the long-term effects need to be evaluated and more studies are needed. Until now, information on the quantitative effects of Pisha sandstone content on solute transport in sandy soil is still inadequate.

Some solutes such as the inert non-adsorbed Br⁻ and Cl⁻, and adsorbed K⁺ and Na⁺, are used as transport tracers in negatively charged soils. Regardless of the solute used, valuable information on solute transport can be deduced from breakthrough curves (BTCs) (Hillel, 1998). In order to study the effect of soil structure on solute transport, two models have been used to study BTCs of inert non-adsorbed solutes: the convection dispersion equation model (CDE) and the two-region model (i.e., mobile-immobile water content model) (T-R). Work by Abbasi et al. (2003) showed that CDE can predict solute transport parameters more accurately than T-R in homogeneous soils. However, Ventrella et al. (2000) and Beibei et al. (2009) found that the T-R model estimates transport parameters somewhat better than CDE when studying a heterogeneous fine-textured soil or loess-containing rock fragments. The two-site model (T-S) is always used to study the BTCs of adsorbed solutes such as K⁺ and Na⁺ (Toride et al., 1995).

The objectives of this study were to determine the effects of Pisha sandstone amendments on the transport of bromide and sodium in sandy soils. Bromide and sodium were chosen because they are representative inert non-adsorbed and adsorbed solutes, respectively. The study was focused on the identification of solute transport processes and the determination of parameters fitted to different models, and this work attempted to identify the factors that influence the solute transport characteristics.

2. Materials and methods

2.1. Materials and analysis

Aeolian sandy soil and Pisha sandstone were collected at the towns of Dalu (111°22'6.4" E, 40°2'45.7" N) and Nuanshui (110°34'34.3" E, 39°44'23.6" N), both of which are located in Jungar Banner, the Inner Mongolia Autonomous Region in northwest China. The soil samples were air dried and sieved through a 2-mm mesh. The properties of the selected soils are shown in Table 1. Soil organic matter was determined according to the dichromate oxidation method of Walkley-Black (Page et al., 1982); particle size distribution was determined by laser diffraction using a Mastersizer 2000 (MS-2000, Malvern, Britain); and the cation exchange capacity (CEC) was determined by shaking 1 mm of air-dried soil with 1 M NH₄OAc at PH 7.0. Exchangeable cations (K⁺ and Na⁺) were analyzed by flame spectrophotometry (Blakemore, 1987). Soil pH was measured with a soil: water ratio of 1:2.5 using an ion pH meter (Lei-ci PXSJ-216F, Shanghai REX Instrument Factory, China).

Air-dried fine sandy soil samples were thoroughly mixed with Pisha sandstone to obtain five different gravimetric contents of Pisha sandstone (0, 16.7, 25, 50, and 100%). The natural bulk densities of sandy soil and Pisha sandstone are approximately 1.60 and 1.40 g/cm³, respectively. Mixtures with bulk densities of 1.60, 1.57, 1.55, 1.50 and 1.40 g/cm³ were then uniformly packed into Plexiglas columns (height of 24.0 cm, inner diameter of 7.0 cm). The perforated bases of the columns were covered with a coarse filter paper to prevent the soil mixtures from flowing with the solution. The surfaces of the soil mixtures were covered with a circular filter paper to reduce the disturbance caused by the inflowing solution. The well-packed soil columns were allowed to stand for 3 days and then were placed in a deionized water sink until the soil was completely saturated throughout the vertical length of the column.

Vertical soil column solute transport experiments were carried out under steady-state flow conditions, and 0.05 M NaBr was used as a tracer. Flow experiments were carried out by rapidly establishing and then maintaining a constant 2.9-cm head of the tracer solution on the surface of the soil using a Mariotte bottle. The effluent was collected continuously in 30-ml volumetric flasks at timed intervals. The effluent samples were then analyzed by an ion meter (Lei-ci PXSJ-216F, Shanghai REX Instrument Factory, China) with Br⁻ and Na⁺ ion selective electrodes (ISE) to determine the Br⁻ and Na⁺ concentrations until they attained stable levels (close to 0.05 M). The experimental temperature was controlled at 20 ± 3 °C, and the relative humidity was not controlled but remained at $40 \pm 10\%$.

2.2. Theory and model

The analysis of solute transport in porous media was based on a simplified convection dispersion equation (CDE) (Kasten et al., 1952; Lapidus and Amundson, 1952):

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - V \frac{\partial c}{\partial x} \quad (1)$$

where R is the retardation factor; C is the concentration of solute in the liquid phase; t is the flow time; V is the pore water velocity; x is the flow distance; and D is the dispersion coefficient.

The dispersivity (λ) and the Peclet number (Pe) were calculated by using derived values of the dispersion coefficient from the CDE model, defined by the following equations:

$$\lambda = \frac{D}{V} \quad (2)$$

$$Pe = \frac{LV}{D} = \frac{l}{\lambda} \quad (3)$$

Table 1a

Selected properties of the sandy soil and Pisha sandstone (International soil science society textural class).

Material	Texture	Clay (%)	Silt (%)	Sand (%)	PH	CEC (cmol kg ⁻¹)	Organic matter (g kg ⁻¹)
Sand soil	Sand	6.767	7.055	86.178	8.36	3.86	2.93
Pisha sandstone	–	15.234	24.09	60.676	9.22	45.79	1.74

Table 1b

Mineral properties of the sandy soil and Pisha sandstone.

Material	Quartz (%)	Montmorillonite (%)	Feldspar (%)	Calcite (%)	Dolomite (%)	Kaolinite (%)	Amphibole (%)
Sand soil	82	–	10	2	–	4	2
Pisha sandstone	57	30	10	0	3	–	–

The two-region model (T-R) was given by Van Genuchten and Wagenet (1989):

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D \frac{\partial^2 C_m}{\partial x^2} - \mu_m \theta_m \frac{\partial C_m}{\partial x} \quad (4)$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \omega (C_m - C_{im}) \quad (5)$$

$$\theta = \theta_m + \theta_{im} \quad (6)$$

where θ_m is the volumetric water content in the mobile region; θ_{im} is the volumetric water content in the immobile region; C_m is the concentration in the mobile region; C_{im} is the concentration in the immobile region; D is the dispersion coefficient; μ_m is the pore water velocity in the mobile region; t is the flow time; x is the flow distance; and ω is the mass transfer coefficient.

The effluent concentration was considered to be the flux-averaged concentration of the soil column, so the initial and boundary conditions were taken as:

$$C_i = 0; \quad 0 < x < l, \quad t = 0 \quad (7)$$

$$\mu_i C_0 = -D_i \frac{\partial C_i}{\partial x} + \mu_i C_i; \quad x = 0, \quad t > 0 \quad (8)$$

$$\frac{\partial C_i}{\partial x} = 0; \quad x = l, \quad t > 0 \quad (9)$$

where C_i is the initial concentration in the mobile region; μ_i is the pore water velocity in the mobile region; C_0 is the initial concentration in the soil column; D_i is the dispersion coefficient of the mobile region; l is the length of the soil column; and t is the flow time. The analytical solutions for the two models can be found in Van Genuchten (1981).

The two-site model (T-S) has been formulated to account for either sorption-related or transport-related nonequilibrium. The model assumes sorption at 2 sites, i.e. at Type 1 sites, sorption is instantaneous and described by an equilibrium sorption isotherm; sorption is time-dependent and follows first-order kinetics at Type 2 sites, the rate-limiting step being either chemical or diffusive (Brusseau et al., 1991). If dimensionless parameters are used, the model equations are given by Nkedi-Kizza et al. (1984):

$$\beta R \frac{\partial C_1}{\partial T} = \frac{1}{Pe} \frac{\partial^2 C_1}{\partial Z^2} - \frac{\partial C_1}{\partial Z} - \omega (C_1 - C_2) - \mu_1 C_1 \quad (10)$$

$$(1 - \beta) R \frac{\partial C_2}{\partial T} = \omega (C_1 - C_2) \quad (11)$$

$$\beta = \frac{\theta + f \rho_b K_d}{\theta + \rho_b K_d} \quad (12)$$

$$\omega = \frac{\alpha(1 - \beta)RL}{v} \quad (13)$$

$$\mu = \frac{L\mu_{liq}}{v} \quad (14)$$

where the subscripts 1 and 2 refer to equilibrium and nonequilibrium sites, respectively; T is the flow time; Z is the flow distance; Pe is the Peclet number; β represents the fraction of instantaneous solute retardation; ω describes the ratio of hydrodynamic residence time to the characteristic time scale for sorption; f is the fraction of Type 1 sites and α (h⁻¹) is the first-order rate for kinetics at Type 2 sites.

2.3. Statistical analyses

The solute transport parameters were estimated by the CXTFIT program contained in the STANMOD software package (Parker and Van Genuchten, 1984; Toride et al., 1995; Langner et al., 1999).

3. Results

Breakthrough curves were constructed by plotting the relative concentration (C/C_0) against the time and pore volume number (Pv), and the effect of different Pisha sandstone contents on the BTCs of Br⁻ is presented in Fig. 1. Table 2 shows the fitting parameters of the CDE and T-R models. Even when the Pisha sandstone content was as great as 100%, smooth BTCs that followed similar trends to those typical for the homogeneous soil without Pisha sandstone were obtained. As shown in Fig. 1a, the penetration time increased as the content of Pisha sandstone increased. There was no significant difference in BTCs with different Pisha sandstone contents when plotted against the pore volume numbers (Fig. 1b).

The effects of varying the Pisha sandstone content on the shape and position of Na⁺ BTCs are shown in Fig. 2. As the content of Pisha sandstone increased, the location of the breakthrough curve shifted to the right. Table 3 lists the parameters obtained by fitting the T-S model. Partition coefficients (K_d) were determined from the retardation (R) values.

4. Discussion

4.1. Effect of Pisha sandstone addition on bromide transport

4.1.1. Analysis of Br⁻ BTCs

When the concentration of ions in the effluent solution begins to rise is called initial penetration, and the concentration of ions does not change is called full penetration, while the corresponding time of penetration is called initial or total penetration time, respectively. According to Fig. 1a, the penetration time of Pisha

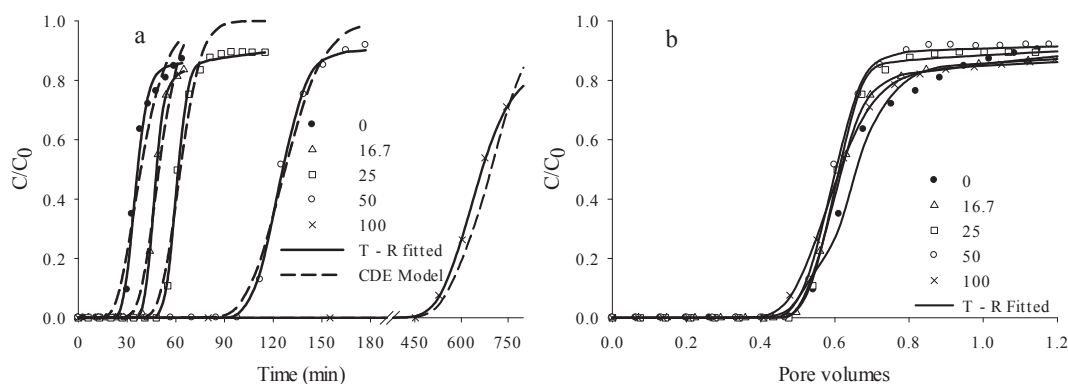


Fig. 1. Observed and estimated bromide BTCs by using CDE and T-R model for samples with different Pisha sandstone contents.

Table 2

Fitted values for parameters using CDE and T-R model from bromide data.

Content (%)	V (cm h ⁻¹)	SSQ		D (cm ² h ⁻¹)		λ (cm)		Pe		β	ω
		CDE	T-R	CDE	T-R	CDE	T-R	CDE	T-R	T-R	T-R
100	1.18 (0.042)	1.49E-01	7.16E-04	0.67 (0.430)	0.23 (0.007)	0.579 (0.384)	0.193 (0.013)	52.72 (43.95)	103.72 (6.86)	0.614 (0.005)	0.0049
50	5.92 (0.805)	6.50E-02	3.67E-03	1.99 (0.513)	0.65 (0.111)	0.355 (0.135)	0.110 (0.004)	62.77 (25.70)	182.36 (6.38)	0.692 (0.007)	0.0080
25	14.12 (0.458)	1.17E-01	3.45E-03	4.19 (0.534)	1.23 (0.033)	0.298 (0.047)	0.087 (0.005)	68.26 (11.01)	230.44 (13.66)	0.754 (0.017)	0.0091
16.7	17.26 (2.843)	1.04E-01	2.47E-04	5.18 (2.455)	1.84 (0.120)	0.284 (0.095)	0.108 (0.011)	76.24 (26.91)	187.17 (18.77)	0.777 (0.009)	0.0079
0	27.72 (6.539)	1.06E-01	2.67E-02	23.28 (0.720)	3.01 (2.241)	0.883 (0.182)	0.126 (0.114)	23.33 (4.92)	385.69 (44.65)	0.692 (0.069)	0.0181

V is average pore velocity; SSQ is the sum of squares residual; D is diffusion coefficient; λ is dispersivity; Pe is Peclet number; β is mobile-immobile partition coefficient; ω is mass transfer coefficient; standard deviation is in the parentheses.

sandstone increased compared with homogeneous sandy soils; in addition, longer breakthrough times were associated with higher contents of Pisha sandstone. This finding indicates that Pisha sandstone additions can hinder the solute transport process, which could be attributed to the different average pore velocities of the materials. In our experiments, a constant 2.9-cm head of 0.05 M NaBr solution was established and maintained on the surface of the soil, ensuring that the same hydraulic gradient was maintained for all soil columns. The largest pore water velocity values were obtained when the Pisha sandstone content was 0% and then decreased with increasing Pisha sandstone content, which is in agreement with the findings presented by She et al. (2014). Several authors have studied the effects of bulk density on solute transport and found that greater bulk soil densities may impede the solute

transport process (Arya and Paris, 1981; Sudicky, 1986; Dianqing et al., 2010). However, in our study, although bulk density decreased with increasing Pisha sandstone content, solute transport was inhibited. This effect can be partly attributed to the typical properties of Pisha sandstone: for example, compared with sandy soil, Pisha sandstone has a low sand content and a high content of montmorillonite, which can reach 30%. Pisha sandstone is thus unstable and can easily expand and disintegrate when encountering water, allowing fine particles to clog the channels that connect large pores. As a result, average pore velocities were decreased in this work, as shown in Table 2.

4.1.2. CDE and the T-R model fitting results

Our experimental data fit both the CDE and the T-R models well. According to Fig. 1a, the T-R model provided a slightly better

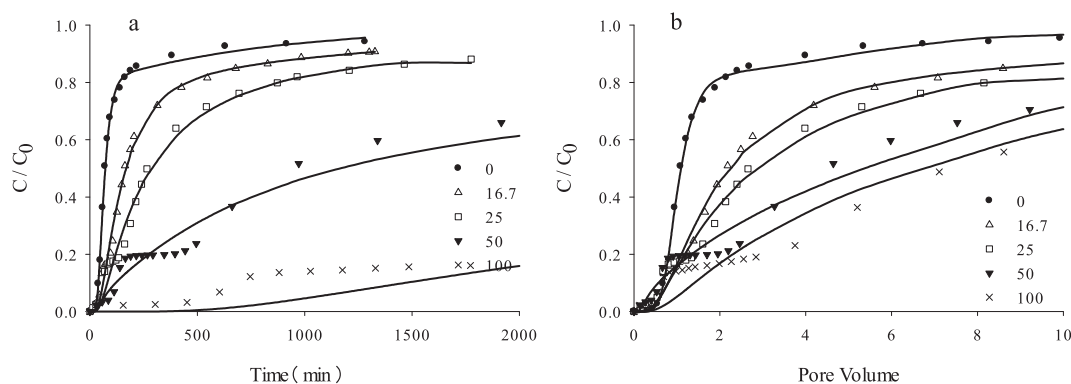


Fig. 2. Observed and estimated sodium BTCs by using T-S model for samples with different Pisha sandstone content.

Table 3
Fitted values for parameters using T-S model from sodium data.

Content (%)	SSQ	R	β	ω	MSE	K_d
100	7.20E-02	94.25 ± 7.75	0.04 ± 0.027	5.600	2.77E-03	31.42 ± 2.611
50	3.79E-02	17.50 ± 6.90	0.31 ± 0.024	1.702	1.72E-03	4.77 ± 1.996
25	2.71E-02	9.68 ± 4.22	0.17 ± 0.013	2.585	1.39E-03	2.32 ± 1.130
16.7	2.09E-02	5.69 ± 0.98	0.40 ± 0.025	0.011	1.17E-03	1.22 ± 0.256
0	4.99E-03	2.14 ± 0.29	0.53 ± 0.002	0.016	2.86E-04	0.28 ± 0.073

$R^2 > 0.974$; SSQ is the sum of squares residual; R is retardation factor; β is parameter associated with fraction of instantaneous solute retardation; ω is ratio of hydrodynamic residence time to characteristic sorption time; K_d is partition coefficient.

fit to the data than the CDE, especially regarding its ability to describe the steep initial increases in relative concentration and the tailing phenomenon. A comparison of the two models is shown in Table 2. SSQ is the residual sum of squares of the fitted and the measured values, and these values indicate that both models predicted relative concentrations of Br^- that fit the experimental data well. However, from either Fig. 1 or Table 2, it can be seen that the T-R model fits the experimental data slightly better than the CDE, which is in agreement with Beibei et al. (2009). The main reason for this finding could be the greater number of parameters used in the T-R model than in the CDE, which would have contributed to a more accurate description of the solute transport processes (Beibei et al., 2009).

Table 2 lists the dispersion coefficients (D) obtained by fitting the CDE and the T-R models. The values followed the same trend for both models and decreased with increasing Pisha sandstone content. This observation can be attributed to the different average pore velocities in the soils. When comparing the two models, the D values obtained from the CDE model were more than twice as great as those obtained from the T-R model. The main reason for this result is that the CDE combines the effects of solute exchange between the mobile and immobile regions into one term (i.e., the equivalent dispersion coefficient) while the processes of hydrodynamic dispersion and diffusional exchange are treated separately by the T-R model (Zhou et al., 2010).

After obtaining the values of D from the fits with both models, we calculated the dispersivity (λ) and reported the results in Table 2. The dispersivity, λ , is an experimental parameter, and can be thought of as an indicator of local solute mobility in a soil. Previous studies found that the values of λ in coarse-textured and homogeneous soils are often less than in fine-textured and heterogeneous soils (Perfect et al., 2002; Asghari et al., 2011). In our study, the λ values of the columns containing soil/sandstone mixtures were less than those of homogeneous aeolian sandy soil and homogeneous Pisha sandstone columns, which is in agreement with Asghari et al. (2011). The main reason may be that the soil/sandstone mixtures have a heterogeneous pore structure. There are more macroporosities in aeolian sandy soil and small porosities in Pisha sandstone. When soil and sandstone mixed together, the pore structure became complicated and heterogeneity. This evidence indicates that Pisha sandstone can be treated as a soil conditioner similar to polyacrylamide (PAM) or cattle manure and hence can be used to reduce dispersivity. However, Beibei et al. (2009) and Zhou et al. (2010) found that the λ values of soil with rock fragments or coal gangue were larger than those of homogeneous soil. This observation can be attributed to the addition of different rock types; the Pisha sandstone was sieved through 2-mm meshes, as were the soil samples in our study, although the rock diameters were larger than 2 mm in their studies. Furthermore, the grain sizes of Pisha sandstone are similar to those of sandy soil to a certain extent. The data in Table 2 show that the dispersion values obtained from the CDE were larger than those obtained from the T-R. To further investigate the relationship between the values obtained by fitting the CDE and T-R models, a

linear regression analysis was carried out. According to the results, there was a significant ($p < 0.05$) positive correlation ($R^2 = 0.843$) between the values obtained using the two models (Fig. 3).

The Peclet number (Pe) is a dimensionless number that can be used to represent the convection and diffusion ratio. As the value of Pe increases, the convective transport ratio increases. In this study, the values of Pe were far greater than 1, indicating that convection was the main component of transport. The recorded Pe values of the soil and sandstone mixtures were larger than those of homogeneous sandy soil or homogeneous Pisha sandstone for both models, although the values predicted by the T-R model were a factor of at least 1.9 higher than those yielded by the CDE model. This could be attributed to the different dispersion values.

The mobile-immobile partition coefficient (β) obtained by fitting the T-R model represents the fraction of solute present in the mobile region under equilibrium conditions (Schulin et al., 1987). According to Table 2, the β values of the homogeneous sandy soil column and Pisha sandstone column were less than those of the soil/sandstone mixtures. In this case, a trend was observed: the value of β decreased with increasing Pisha sandstone content, indicating a decreasing trend in the fraction of mobile water and effective porosity. The main reason for this finding could be that the Pisha sandstone easily disintegrated in the presence of water, resulting in the blocking of some pore spaces, reducing the effective porosity as a result. The mass transfer coefficient (ω) obtained from the T-R model is conceptually related to the dispersivity, and there is no regular trend in ω . The values of β were not close to 1, indicating that the transport process is, to some extent, affected by the physical nonequilibrium mechanism. However, all values of β were larger than 0.6, indicating that the mobile water accounts for a major proportion of the total soil water and equilibrium transport conditions can be considered (Gonzalez and Ukrainczyk, 1999). Meanwhile, the values of ω were very small (nearly equal to 0). Hence, effectively, no mass exchange occurred between the mobile region and the immobile region.

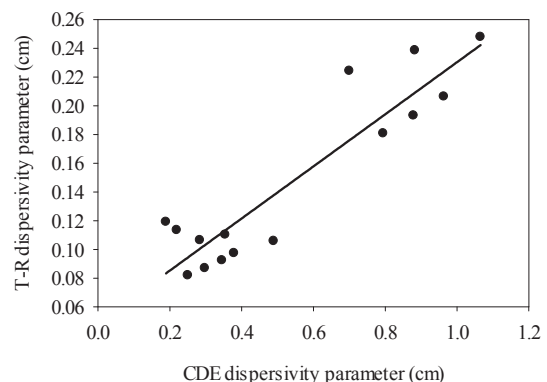


Fig. 3. Correlation between CDE and T-R dispersivity parameter ($\lambda_{\text{T-R}} = 0.1814 \lambda_{\text{CDE}} + 0.049$, $R^2 = 0.843$, $P < 0.05$).

4.2. Effect of Pisha sandstone addition on sodium transport

4.2.1. Analysis of Na^+ BTCs

Fig. 2 shows the effect of varying the Pisha sandstone content on the BTCs of Na^+ . It can be seen that smooth BTCs that followed a similar trend to those typical for a homogeneous soil without the addition of Pisha sandstone were obtained. BTCs were also constructed by plotting the relative concentration (C/C_0) against the time and the pore volume number (Pv). It can be seen in Fig. 2a that the penetration time increased with increasing Pisha sandstone content, which was similar to the results obtained for the Br^- BTCs. This is due to the reduction in average pore velocity with increasing Pisha sandstone content. Compared with the corresponding Br^- BTCs, the initial and total penetration times were higher for the Na^+ BTCs. The main reason for this result is that the cationic adsorption of the soils resulted in a retardation effect. Fig. 2b shows the BTCs constructed by plotting the relative concentration (C/C_0) against the pore volume (Pv). At the same pore volume, the relative concentration decreased with increasing Pisha sandstone content, indicating that the addition of Pisha sandstone hinders Na^+ transport. As shown in Fig. 2a and b, the initial relative concentrations were not equal to 0, and thus, the model fit was not very good. This outcome can be attributed to the dissolution of a small amount of sodium from the matrix into the water fraction, resulting in a slightly higher concentration of sodium in the effluent solution. Wang et al. (2013) also found non-zero initial concentrations in the BTCs of ammonium.

4.2.2. The T-S model fitting results

The BTCs are skewed to the right, exhibiting a tailing phenomenon that implies the existence of nonequilibrium conditions during transport through the columns (Fig. 2). Because the transport-related nonequilibrium was assumed to be nearly negligible, the observed nonequilibrium is likely due to a sorption-related process (Montoya et al., 2006). The T-S model provided by STANMOD had an acceptable fit with the observed data ($R^2 > 0.974$). Table 2 shows some of the parameters obtained by fitting the T-S model, and the partition coefficient (K_d) was calculated from the retardation factors (R).

The R value of Pisha sandstone was up to 44 times higher than that of the sandy soil, indicating that Pisha sandstone can retard sodium transport. R increased with increasing Pisha sandstone content, which may be due to the increasing CEC. A study by Kim et al. (2006) found that R for benzene transported in a sandy soil increased with decreasing flow velocities. The average pore velocity influences the contact time between the solutes and the porous medium. That is, a low average pore velocity increases the contact time of Na^+ with soil particles, allowing Na^+ to reach an adsorption dynamic balance more easily while contributing to an increased amount of Na^+ adsorption overall. To study further the effect of CEC on R , correlation and regression analyses were carried out, as shown in Fig. 4. A significant ($p < 0.01$) positive correlation was obtained between R and CEC, and the relationship was fit as a power function. K_d followed a similar trend as R . The K_d values of Pisha sandstone were up to 100 times those of the sandy soil, implying that Pisha sandstone had a stronger capacity for Na^+ adsorption. Similar results were also found by Jing et al. (2014), who observed that Pisha sandstone has a relatively large capacity for the adsorption of Pb.

The parameter β obtained from the T-S model fit is a fraction factor that can reflect the ratio of the instantaneous equilibrium adsorption sites to all the adsorption sites (including instantaneous equilibrium and kinetic adsorption sites) in the soil. The values of β ranged from 0.04 to 0.53, meaning that chemical nonequilibrium adsorption influences Na^+ transport; in addition, a portion of the sorption sites did not participate in instantane-

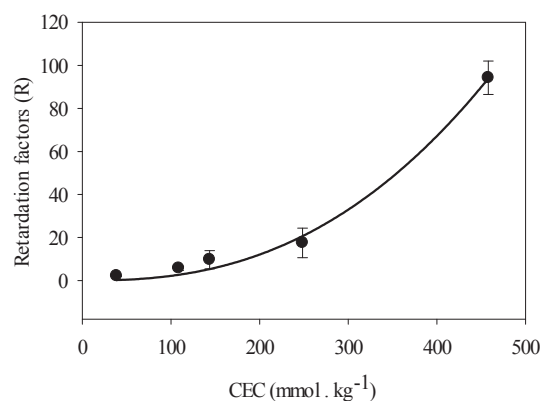


Fig. 4. Correlation between CEC and retardation factor (R) ($R = 2.4325E-005 \cdot V_{\text{CEC}}^{2.4755}$, $R^2 = 0.993$, $P < 0.01$).

ous adsorption (Huo et al., 2013). Furthermore, the values of β increased significantly with increasing contents of Pisha sandstone (except for a sandstone content of 25%), indicating that Pisha sandstone can increase the degree of chemical nonequilibrium. In this case, ω ranged from 0.011 to 5.600, which provided additional evidence that nonequilibrium adsorption processes govern Na^+ transport. The values of ω also increased with increased Pisha sandstone additions. This result could be attributed to the decrease in average pore velocity obtained with increasing Pisha sandstone fractions.

5. Conclusion

In this study, the influence of Pisha sandstone on bromide and sodium transport was investigated in a sandy soil. The results showed that the incorporation of Pisha sandstone can inhibit the transport of both Br^- and Na^+ . The application of Pisha sandstone can also prevent the early breakthrough of both tracers by decreasing the saturated hydraulic conductivity relative to the sandy soil columns. The strength of the retardation increased with higher Pisha sandstone content. The BTCs of Br^- were accurately described by both the CDE and T-R models, and the T-R model fit the experimental data slightly better than the CDE. The T-S nonequilibrium model accurately fit the data observed for the transport of Na^+ . Pisha sandstone retarded the breakthrough of Na^+ not only by decreasing the saturated hydraulic conductivity but also by increasing the adsorption capacity of the sandy soil. The CEC value of Pisha sandstone was 11 times larger than that of the sandy soil. We found that the incorporation of Pisha sandstone increased the degree of chemical nonequilibrium in the soil columns.

This study provides evidence that Pisha sandstone can successfully retard solute transport in a sandy soil, in addition to enhancing our understanding of the role of Pisha sandstone in water movement and solute transport in the soils in Shanxi, Shaanxi and Inner Mongolia's border region. Further and systematic research is required, such as transport under different velocity conditions. The distribution and range of Pisha sandstone in soils in nature is complex, and the findings of this and similar studies must be transferred to the field.

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